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(54) Process for the carbonylation of butadiene or a butadiene derivative

(57) A process for the carbonylation of butadiene or a butadiene derivative in the presence of carbon monoxide and an alcohol or water and a catalyst system comprising palladium, a carboxylic acid and a monodentate phosphine ligand is described in which the amounts of reactants during the carbonylation process are such that the molar ratio of butadiene or butadiene derivative to palladium in the reaction mixture is less than 70:1, the molar ratio of carboxylic acid to palladium is greater than 10:1 and the molar ratio of alcohol or water to butadiene or butadiene derivative is less than 2:1.

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Description

The invention relates to a process for the carbonylation of butadiene or a butadiene derivative in the presence of carbon monoxide and an alcohol or water and a catalyst system comprising palladium, a carboxylic acid and a monodentate phosphine ligand.

A carbonylation reaction according to this invention means every reaction between an unsaturated substrate and a hydroxy group containing reactant and carbon monoxide, in which an acid or ester compound is obtained.

US-A-5028734 describes a batch wise carbonylation of butadiene in the presence of ethanol and a catalyst system comprising palladium, triphenyl phosphine and 2,4,6-trimethylbenzoic acid. The molar ratio of butadiene and palladium was about 90:1 at the start of the carbonylation. The molar ratio of acid and palladium was 7.5:1 and the molar ratio of alcohol and butadiene was 2.7:1. A disadvantage of this process is that the selectivity to pentenoate ester is low. The selectivity to methyl pentenoate was only about 75%. Most of the by-products were nonadienoates.

An object of the present invention is to provide a process for the carbonylation of butadiene or a butadiene derivative wherein the selectivity to pentenoate ester or acid is higher than can be obtained with the process described in US-A-5028734.

This aim is achieved in that the amounts of reactants are maintained, substantially during the whole process, such that the molar ratio of butadiene and palladium in the reaction mixture is less than 70:1 and the molar ratio of carboxylic acid and palladium is higher than 10:1, and the molar ratio of alcohol or water to butadiene or butadiene derivative is less than 2:1.

When the process is performed in the above described manner the selectivity to pentenoate ester or acid is considerably improved. An additional advantage is that the catalyst system is stable for a longer period of time and that the catalyst system may be reused several times without loss of catalytic activity provided that the measures are taken as described below. A further advantage is that no halogen containing compounds and/or organic nitrogen containing base is needed to achieve favorable selectivities.

In the aforementioned US-A-5028734 another method of carbonylation is described in which, instead of the monodentate phosphine ligand, a multidentate phosphine ligand, such as 1,4-bis(diphenylphosphino) butane, is used. The improvement over the use of monodentate phosphine ligands was a better selectivity to pentenoate ester. However, in the process of US-A-5028734, relatively complex multidentate phosphine ligands are needed to achieve the improved selectivity. Another disadvantage of this process is that the multidentate phosphines decompose during the carbonylation reaction. The advantage of the process according to the present invention is that a comparable improved selectivity to pentenoate ester can be achieved without having to use these multidentate phosphine ligands.

When the carbonylation is performed in the presence of water, as the hydroxy group containing reactant, the main product will be the pentenoic acid. In case an alcohol is used, as the hydroxy group containing reactant, a pentenoate ester will be formed as the main product.

The pentenoate ester which is formed during carbonylation of butadiene and an alcohol will actually be a mixture of 2-, 3- and 4-pentenoate esters. An additional advantage of the process according to the invention is that less 2-pentenoate ester is formed compared to the process of US-A-5028734. This is advantageous when such a mixture is used in the hydroformylation of pentenoate ester to the terminal 5-formylvalerate ester with a rhodium-based catalyst system, such as described in, for example, US-A-5264616, the complete disclosure of which is incorporated herein by reference. The 2-pentenoate ester in the mixture has an adverse effect on the selectivity to 5-formylvalerate ester as is clear from US-A-5264616.

The alcohol is, for example, an organic compound with 1 to 20 carbon atoms with one or more hydroxy groups. The organic compound can be an aliphatic, cycloaliphatic or aromatic compound. These compounds include, among others, phenol, cresol, tert-butyl catechol and cyclohexanol. By preference, the alcohol is an aliphatic alcohol, in which the aliphatic group R is a linear or branched alkyl group. The alkyl group has preferably 1 to 6 carbon atoms. Alkanols of the formula ROH are useful herein, and include methanol, ethanol, propanol, isopropanol, butanol, tert-butanol, pentanol and hexanol. Most preferably methanol or ethanol is used as the alcohol. A substituted alcohol can be used such as, for instance, an ether-substituted alcohol, of which the methyl ether of ethylene glycol is exemplary.

The molar ratio of alcohol or water to butadiene in the process according to the invention is less than 2:1. Most preferably this ratio is lower than 1.5:1. Preferably the molar ratio alcohol or water and butadiene is greater than 0.5:1. More preferably the amount of alcohol or water is at least the stoichiometric amount in relation to butadiene because then high yields to the desired product can be achieved. The molar ratio alcohol or water and butadiene is thus preferably 1:1 or higher.

The monodentate phosphine ligand is preferably a compound according to the following general formula:

$$R^1 - \underset{}{\overset{\overset{\displaystyle R^2}{|}}{P}} - R^3 \qquad (1)$$

wherein R^1, R^2 and R^3 each individually represent an optionally substituted organic group. The organic group can be, for example, a C_1-C_{20} alkyl group, a C_2-C_{20} alkenyl group, a C_6-C_{18} aryl group or a cyclic group with 4-12 carbon atoms in which the ring of the cyclic group also contains one or more heteroatoms such as, for example, nitrogen. Exemplary alkyl groups include, for example, methyl, ethyl, isopropyl, tert-butyl and cyclohexyl. An exemplary alkenyl group is butenyl. Exemplary cyclic groups containing heteroatoms include, for instance 6-methyl-2-pyridyl and 4,6-dimethyl-2-pyridyl. Preferably at least one of the organic groups R^1, R^2 and R^3 is a C_6-C_{18} aryl group and more preferably a C_6-C_{14} aryl group. Aryl groups include naphtyl and phenyl. The organic group can be substituted with for example, halogen atoms, for example Cl, Br or F, or with C_1-C_6 alkyl, C_6-C_{18} aryl, C_1-C_6 alkoxy, carboxy, carbalkoxy, acyl, trihalogenmethyl, cyano, dialkylamino, sulphonylalkyl or alkenoyloxy groups. Substituents may be groups with electron withdrawing or electron donating properties.

Examples of monodentate phosphine ligands include tri-p-tolylphosphine, tri-p-methoxyphenyl phosphine, diphenylpentylphosphine and dimethylphenylphosphine. Preferably triphenylphosphine is used because this compound is generally readily available.

The molar ratio of monodentate phosphine ligand to palladium is preferably greater than 5:1. Normally this ratio will be below 50:1. When this ratio is too low the catalytic effect of the catalyst system is weaker and by-products such as vinyl cyclohexene and high-molecular weight products may form. Multidentate phosphine ligands may, if desired, be present during the carbonylation reaction. Preferably these multidentate phosphine ligands are not used as a co-ligand because these ligands tend to decompose during the reaction as described above.

As used herein, the term butadiene derivative means those compounds which yield pentenoate ester or pentenoic acid as the major product when carbonylated with the process according to the invention. If no statement is made to the contrary, all references to butadiene shall also include butadiene derivatives in this description. It is also possible to carbonylate mixtures of butadiene and butadiene derivatives with the process according to the invention. Although butadiene derivatives are readily employed in the present process, butadiene is preferred because of its availability. The butadiene can be used in pure form, or in an admixture with aliphatic compounds. For instance, an exemplary of such admixture is the C_4-cut obtained in a steam cracker process. The C_4-cut can comprise butadiene plus 1-butene, 2-butene, and/or isomeric butynes.

Preferred butadiene derivatives are represented by the following general formulae:

$$CH_3 - CH = CH - CH_2 - X \qquad (2)$$

$$CH_3 - CHX - CH = CH_2 \qquad (3)$$

wherein X is an organic group with 1 to 20 carbon atoms or an inorganic group. Examples of suitable organic groups include $-OR^4$ or $-OC(O)R^5$ groups, in which R^4 and R^5 can be, for example, a C_1-C_6 alkyl, C_2-C_6 alkenyl, a C_6-C_{14} aryl a C_7-C_{14} aralkyl or a C_7-C_{14} alkaryl group. Examples of these groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl, pentyl, cyclopentyl, cyclohexyl, hexyl, propenyl, butenyl, pentenyl, phenyl, naphthyl, benzyl or tosyl. Examples of other suitable organic groups or inorganic groups are -OH, $-H_2PO_4$, $-PR^6R^7$, $-NH-CO-R^8$, $-NH_2$, and $-SR^9$, in which R^6, R^7, R^8 and R^9 can be the same as defined above for R^4 and R^5.

Butadiene derivatives include 1-methoxy 2-butene, 3-methoxy 1-butene, 1-ethoxy 2-butene, 3-ethoxy 1-butene, isomeric butenyl pentenoate, 1-butene 3-carbonate, 2-butene 1-carbonate, 3-hydroxy 1-butene, and 1-hydroxy 2-butene.

Methods of making alkoxy butenes, e.g. methoxy butene, are described in US-A-4343120 and US-A-4590300, the complete disclosure of which are incorporated herein by reference.

All inert solvents are in principle suitable as an additional solvent, but it is also possible to use an excess of one of the reactants or by-products in such an amount that a suitable liquid phase is formed. Suitable reactants or by-products are the pentenoate ester, C_9-esters and high boiling by-products. Examples of inert solvents are sulphoxides and sulphones, such as dimethyl sulphoxide, diisopropyl sulphone; aromatic solvents, such as benzene, toluene, xylene; esters, such as methyl acetate, methyl valerate, pentenoate esters and butyrolactone; ketones, such as acetone or methylisobutyl ketone; ethers such as anisole, trioxanone, diphenyl ether and diisopropyl ether; and mixtures of these solvents. Preferably, diphenyl ether is used as additional solvent.

The palladium can be present in the reaction mixture as a heterogeneous palladium compound or as a homogeneous palladium compound. However, homogeneous catalyst systems are prefered. Since palladium in situ forms a complex with the phosphine ligand, the choice of the initial Pd compound is in general not critical. Homogeneous palladium compounds include, for instance, palladium salts of nitric acid, sulphonic acid, alkane carboxylic acids with not more than 12 carbon atoms or hydrogen halogenides (F, Cl, Br, I). Metallic palladium can also be used. Examples of homogeneous palladium compounds are $PdCl_2$, $PdBr_2$, PdI_2, Na_2PdI_4, K_2PdI_4, $PdCl_2$(benzonitrile)$_2$ and bis(crotyl-palladium chloride). Another group palladium compounds are halogen-free palladium complexes such as palladium acetylacetonate (Pd(acac)$_2$), palladiumacetate, palladiumnitrate $Pd(NO_3)_2$, tetrakis(triphenyl phosphine)palladium,

and di-palladium-tris-(dibenzylideneacetone) $Pd_2(dba)_3$. An example of a suitable heterogeneous palladium compound is palladium on an ion exchanger, such as, for instance, an ion exchanger containing carboxylic acid groups. Ion exchangers containing carboxylic acid groups are commercially available under the brand names Amberlite IRC 50 and Amberlite IRC 84 (Rohm & Haas). Another possible heterogeneous catalyst is an immobilized phosphine on carrier catalyst, in which the palladium forms a complex with the immobilized phosphine (immobilized phosphine is the phosphine ligand of the catalyst system). Carriers include polystyrene, polyacrylamide, or silica.

The palladium concentration in the reaction mixture is preferably as high as possible because then the rate of reaction per unit of reactor volume will be higher. The upper limit for a homogeneous catalyst system will normally be determined by the solubility of palladium in the reaction mixture and, for example, will depend on the specific palladium compound used as discussed above. This upper limit can easily be determined by one skilled in the art.

Preferably the butadiene/palladium molar ratio is greater than 1:1, and more preferably is greater than 2:1. The butadiene/palladium molar ratio is less than 70:1, and preferably is less than 50:1.

To achieve such low butadiene/palladium molar ratios, the butadiene is preferably continuously supplied to the carbonylation reaction at a rate of at most 100 mol butadiene per hour per mol palladium present during the carbonylation. More preferably this rate is less than 80 mol butadiene per hour per mol palladium.

The carboxylic acid is preferably an organic compound with 1 to 30 carbon atoms. The pKa of the acid is preferably greater than 2 measured in an aqueous solution of 18°C. The pKa is preferably less than 5.0. These organic compounds may be substituted with hydroxy, C_1-C_4 alkoxy, for example methoxy, amine or halogenide groups, for example Cl, I and Br. Exemplary carboxylic acids are benzoic acid, acetic acid, valeric acid, butanoic acid cyclohexylpropionic acid or nonanoic acid. It has also been found that acids corresponding with the ester (by-)products of the present invention can be used. The use of these acids is advantageous because they are readily obtainable, by hydrolysis of these ester (by)products. Examples of these acid hydrolysis products are nonadienoic acid, pentenoic acid, 1-butene-2-carboxylic acid and methyl-substituted butenoic acid. Preferably the acid is a sterically hindered carboxylic acid having a pKa of less than 4.5. Exemplary sterically hindered carboxylic acids are sterically hindered benzoic acids, for example the C_1-C_4 alkyl substituted benzoic acid, for example 2,6-dimethylbenzoic acid, 2,4,6-trimethyl benzoic acid and hydroxy substituted benzoic acid, for example meta- and parahydroxybenzoic acid and other substituted benzoic acids, for example 2,6-difluorobenzoic acid or 2,4,6-tribromobenzoic acid.

The carboxylic acid is preferably pentenoic acid when pentanoate ester is the desired end product. Under some carbonylation conditions the carboxylic acid of the catalyst system is consumed during the reaction, e.g., wherein the carboxylic acid reacts with the alcohol to form the corresponding ester. By using pentenoic acid as co-catalyst, the desired end product (the pentenoate ester) is obtained as the reaction product of the pentenoic acid. Fresh pentenoic acid needed to replace the thus consumed pentenoic acid can be prepared by hydrolysis of a portion of the pentenoate ester obtained in the process according to the invention.

Another preferred carboxylic acid is a nine-carbon carboxylic acid which can be saturated or unsaturated. An example of nine-carbon saturated carboxylic acid is nonanoic acid.

An example or nine-carbon unsaturated carboxylic acid is nonadienoic acid. The corresponding ester is formed as by-product in the process according to the invention. Thus the acid can be formed by a simple hydrolysis of this ester by-product.

Such a hydrolysis can be performed in a separate step, for example by contacting some of the pentenoate ester with an acid ion exchange resin in the presence of water. Such contacting can be performed in, for example, an on-purpose unit operation (specific designed process step or equipment) or in one of the distillation columns used for separating the pentenoate ester from one of the other components of the catalyst system present in the effluent of the reactor. It has been found that the addition of small amounts of water to the carbonylation reaction will result in a stable concentration of pentenoic acid in a continuous process. The amount of water needed will depend on the amount of pentenoic acid being consumed by esterification during the carbonylation. The rate of esterification will depend on the reaction conditions which are selected and can be easily determined by analyzing the reaction mixture leaving the reactor. If a carboxylic acid other than pentenoic acid is used, the esters formed can also be hydrolyzed as described above in a separate hydrolysis to the original acid, which acid can be reused in the process.

When water is used as the hydroxy group containing compound in the carbonylation reaction, pentenoic acid is the main product, and esterification of the acid co-catalyst cannot occur. In such a process the pentenoic acid formed may also serve as the acid co-catalyst according to the process according to the invention. Adding a different carboxylic acid is however possible. Examples of these carboxylic acids are the same as described above.

The molar ratio of carboxylic acid to palladium is greater than 10:1 in the process according to the invention. Apart from practical considerations, there is no upper limit to this ratio. Because, as explained above, the palladium concentration is preferably as high as possible, this will result in a practical upper limit. For example, a practical upper limit is 100:1. Furthermore it has been found that the optimum carboxylic acid to palladium ratio depends on the specific carboxylic acid which is used as co-catalyst. It has been found, for example, that about twice as much (mol) pentenoic acid per mol palladium than sterically hindered benzoic acid per mol palladium is preferred to achieve favorable results.

The carboxylic acid may serve as the solvent of the carbonylation reaction.

The amounts of reactants as specified herein should preferably be maintained substantially during the whole process. By preference, substantially during the whole process means during more than 90% of the process as expressed in residence time.

The temperature of the carbonylation is preferably between 25°C and 200°C. The pressure is not particularly critical and generally ranges between 1 MPa and 20 MPa, although it is preferably greater than 2 MPa. An upper limit is not critical. A very high pressure is disadvantageous because the process equipment will become very expensive. A practical and preferred upper limit is therefore about 10 MPa.

The carbon monoxide can be used in a pure form or diluted with an inert gas such as, for example, nitrogen, rare gases or carbon dioxide. In general, more than 5% hydrogen is undesirable, since this can cause hydrogenation of butadiene under the carbonylation conditions. The amount of carbon monoxide is not critical if at least a stoichiometric amount of carbon monoxide relative to butadiene is supplied to the carbonylation reaction.

The reaction mixture may optionally contain one or more polymerization inhibitors. Suitable polymerization inhibitors include quinones, nitro compounds, diphenylamine, tert-butyl catechol and N,N'-naphthyl-p-phenylene diamine.

The carbonylation can be performed batch wise, semi-continuously or continuously.

In a preferred embodiment of the process according to the inveniton the carbonylation is performed on a continuous or semi-continuous basis. An example of a semi-continuous process for the preparation of pentenoate ester is a process in which a stirred tank reactor is filled with a catalyst system, a solvent and possibly reactants and to which tank continuously butadiene and optionally the alcohol and/or make up carboxylic acid are continuously supplied. The rate at which butadiene and alcohol are supplied will be determined by the rate at which butadiene reacts and is consumed in the reaction. The rate at which carboxylic acid or small amounts of water, for an in situ formation of co-catalyst, has to be supplied will depend on the rate of esterification of the carboxylic acid during carbonylation.

Preferably a continuous process is used. An example of reactor system for a continuous process is a series of continuously stirred tank reactors (CSTR) in which a catalyst system, a possible solvent, butadiene, carbon monoxide and alcohol are fed to a first reactor. The various ratios according to the process of the invention can be maintained by controlling the feed rate of the various reactants and catalyst components. The resulting reaction mixture in the first reactor is fed to a second reactor. Fresh butadiene, alcohol and optionally fresh co-catalyst or small amounts of water are fed to the second and further reactors in the appropriate amounts to maintain the desired ratios of the process according to the invention. Instead of a series of CSTR's, a tube reactor can also be used in which, for example, butadiene and alcohol are supplied in intermediate locations along the tube. The catalyst system leaving the last reactor can be separated from the carbonylation products and returned to the first reactor. These reactor systems can also be used when pentenoic acid is the desired product.

Separating the carbon monoxide, butadiene, alcohol and the pentenoate ester from the reaction mixture which comprises the catalyst system can be performed in various ways. Generally the carbon monoxide is separated first from the reaction mixture in, for example, a simple gas-liquid separation unit. The butadiene, alcohol (alcohol may be replaced by water in the following description of the process when pentenoic acid is the main product) and the pentenoate ester can be separated from the reaction mixture containing the catalyst system in one step followed by isolating the pentenoate ester from butadiene and alcohol. Preferably the butadiene and alcohol are separated from the reaction mixture in a separate step followed by the isolation of the pentenoate ester from the remaining reaction mixture. The various compounds can be separated using a variety of techniques such as, for example, by simple flash operation or by distillation. The choice of unit operation is a function of the physical properties of the compounds to be separated.

The remaining mixture containing the catalyst system comprising the ligand, Pd and the carboxylic acid and, for example, high boiling by-products and a solvent if present, are returned to the reaction zone to be used in a further carbonylation. In order to prevent a build up of, for example, high boiling by-products in this circulating reaction mixture, a part of this mixture may be purged and reprocessed to retrieve, for example, palladium and/or the phosphine ligand.

Pentenoic acid or pentenoate ester can be, for example, advantageously used as an intermediate compound in the preparation of ε-caprolactam and adipic acid, raw materials for the preparation of nylon-6 and nylon-6,6, respectively.

The invention is further described in the following non-limiting examples. The conversion (conv.), selectivity (sel.) and activity (act.) mentioned in the examples are defined as follows:

$$\text{conv.} = \frac{\text{converted butadiene (mol)}}{\text{initial amount of butadiene (mol)}} * 100\%$$

$$\text{sel. of pentenoate} = \frac{\text{obtained amount of pentenoate (mol)}}{\text{converted amount of butadiene (mol)}} * 100\%$$

act. = converted amount of butadienen (mol) per mol Pd per hour.

In the foregoing conversion, selectivity and activity determinations, the term converted butadiene means the amount of butadiene which is reacted to (by)products which cannot react under the carbonylation reaction conditions

in any way to the product 2-, 3- and 4-pentenoate ester. These (by)products are, for example, butene, vinylcyclohexene and high boiling products for example C_9-heavies (e.g. nonadienoates and the like) and higher boiling products. Intermediates which can react to pentenoate ester are excluded.

Example I

A 150 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.47 g (2.1 mmol) of Pd(II) acetate, 5.47 g (20.9 mmol) of triphenyl phosphine, 6.0 g (36.6 mmol) of 2,4, 6-trimethyl benzoic acid and 35.6 g of diphenyl ether as a solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Subsequently, under a pressure of 1.0 MPa of CO with stirring at a speed of 1250 rpm, a mixture of 2.49 g (78 mmol) of methanol, 3.91 g (73.5 mmol) of butadiene (BD) and 0.70 g of nonane (internal standard for GC product analysis) was injected under pressure from an injection vessel into the autoclave. The temperature of the reaction mixture was raised to 140°C at a CO pressure of 6.0 MPa. After 10 minutes at this temperature a continuous butadiene and methanol supply to the reactor was started wherein butadiene and methanol were continuously supplied to the reactor at a constant rate of 142 mmol butadiene and 172 mmol methanol per hour. The butadiene supply was thus 68 mol/mol Pd/hr. After 3.0 hours the reaction was stopped and the reaction mixture was analyzed by gas chromatography. The initial start up molar ratio of butadiene/Pd was 35:1. During the operation of this experiment this ratio increased to 43:1.

The butadiene conversion was 82%. The selectivity to methyl pentenoates (MP) was 93%, whereby the selectivity to trans-methyl-3-pentenoate (t-M3P) was 61.1%, to cis-methyl-3-pentenoate (cis-M3P) was 26.9%, to trans-methyl-2-pentenoate (t-M2P) was 4.7%, to cis-methyl-2-pentenoate (cis-M2P) was 0.2%, and to methyl-4-pentenoate (M4P) was 0.1%. The activity was 60 hr^{-1}. 5.4% of the 2,3,6-trimethyl benzoic acid was converted to its methyl ester.

Comparative Experiment A

A 50 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.05 g (0:22 mmol) of Pd(II) acetate, 0.61 g (2.32 mmol) of triphenyl phosphine, 0.26 g (1.6 mmol) of 2,4,6-trimethyl benzoic acid and 27.0 g of diphenyl ether as a solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Subsequently, under a pressure of 1.0 MPa of CO while stirring at a speed of 1250 rpm, a mixture of 3.76 g (118 mmol) of methanol, 5.14 g (95.3 mmol) of butadiene and 0.45 g of nonane (internal standard for GC product analysis) was injected under pressure from an injection vessel into the autoclave. The temperature of the reaction mixture was raised to 150°C at a CO pressure of 6.0 MPa. After 5.0 hours the reaction was stopped and the butadiene and the reaction products were analyzed by gas chromatographic methods. The initial butadiene/palladium ratio was 433:1. During the experiment this ratio decreased to 61:1.

The conversion was 86%. The selectivity to methyl pentenoates was 21%, and the activity was 16 (hr^{-1}). 9% of the trimethyl benzoic acid was converted to its methyl ester.

Comparative Experiment B

A 150 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.182 g (0.81 mmol) of Pd(II) acetate, 2.1 g (8.0 mmol) of triphenyl phosphine, 2.388 g (14.5 mmol) of 2,4,6-trimethyl benzoic acid and 32.4 g of diphenyl ether as a solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Subsequently, under a pressure of 1.0 MPa of CO while stirring at a speed of 1250 rpm, a mixture of 1.75 g (32.4 mmol) of butadiene, 1.24 g (38.9 mmol) of methanol and 0.705 g of nonane (internal standard for GC product analysis) was injected under pressure from an injection vessel into the autoclave. The temperature of the reaction mixture was raised to 140°C at a CO pressure of 6.0 MPa. After 20 minutes at this temperature, a butadiene and a methanol supply at a constant rate of 105 and 116 mmol per hour respectively were started, using Gilson model 302 pumps, thus the butadiene supply was 130 mol/mol Pd/hr. After 5.0 hours the reaction was stopped and the butadiene and the reaction products were analyzed by gas chromatographic methods. The initial butadiene/palladium ratio was 49:1. During the experiment this ratio increased to 220:1.

The conversion was 68%. The selectivity to methyl pentenoates was 64.8%, whereby the selectivity to trans-methyl-3-pentenoate was 43.0%, to cis-methyl-3-pentenoate 19.0%, to trans-methyl-2-pentenoate 2.5%, to cis-methyl-2-pentenoate 0.1%, and to methyl-4-pentenoate 0.1%. The activity was 59 hr^{-1}. 8.7% of the trimethyl benzoic acid was converted to its methyl ester.

Comparative Experiment C

A 50 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.28 g (1.2 mmol) of Pd(II) acetate, 3.2 g (12.3 mmol) of triphenyl phosphine, 2.1 g (12.6 mmol) of trimethyl benzoic acid and 27.2 g of diphenyl ether as a

solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Subsequently, under a pressure of 1.0 MPa of CO while stirring at a speed of 1250 rpm, a mixture of 13.6 g (425 mmol) of methanol, 13.8 g (255 mmol) of butadiene and 0.32 g of nonane (internal standard for GC product analysis) was injected under pressure from an injection vessel into the autoclave. The temperature of the reaction mixture was raised to 150°C at a CO pressure of 9.0 MPa. After 3.0 hours the reaction was stopped and the butadiene and the reaction products analyzed by gas chromatographic methods. The initial butadiene/palladium ratio was 213:1. During the experiment this ratio decreased to 21:1.

The conversion was 90%. The selectivity to methyl pentenoates was 55%, and the activity was 34 (hr^{-1}). 18% of the trimethyl benzoic acid was converted to its methyl ester.

Examples II-XV

Example I was repeated several times, under different reaction conditions (see Table 1). The temperature was 140°C, unless otherwise stated. The results are also listed in Table 1. In all runs 2,4,6-trimethyl benzoic acid was used as co-catalyst, with a molar ratio of 17 versus Pd(II) acetate. Triphenyl phosphine was used as the ligand, with a molar ratio of 10 versus Pd(II) acetate. Methanol was supplied with a molar ratio of 1.2 versus the butadiene feed, as in Example I.

TABLE 1

Ex. num	BD/Pdt=0 (1)	BD/Pd (2)	BD feed (mol/mol Pd/hr)(3)	Time (hr)	Conv. (%)	Sel MP's (%)	Sel M2P (%)	Act. (hr^{-1})
II	44	35	33	4.0	84	94.2	3.0	29
III (4)	43	26	33	6.0	89	93.5	4.2	32
IV (5)	44	23	35	6.0	91	91.9	5.2	34
V (6)	44	20	32	6.0	91	92.6	6.0	33
VI (7)	12	8	18	6.0	86	92.8	7.9	20
VII	23	8	37	6.0	94	97.4	7.6	35
VIII	45	32	37	6.0	88	92.7	4.4	35
IX	44	15	39	4.0	93	93.6	3.7	42
X	44	16	39	4.0	92	94.4	3.8	43
XI	47	14	36	3.1	91	95.8	5.2	44
XII	47	18	37	5.0	92	94.8	6.9	40
XIII	51	47	53	5.0	85	92.1	5.2	48
XIV	29	27	50	4.0	88	94.7	6.2	47
XV	22	15	40	4.5	93	93.7	4.2	39

(1) initial butadiene/palladium ratio
(2) end of experiment-butadiene/palladium ratio
(3) butadiene feed in mol butadiene per mol Pd per hour
(4) pressure was 5.0 Mpa
(5) pressure is 2.5 MPa
(6) temperature was 160°C, pressure was 5.5 MPa
(7) pressure was 5.0 MPa

Example XVI

Example I was repeated, charging the autoclave with 0,453 gram palladium acetate (2.0 mmol), 5.3 gram triphenylphosphine (20 mmol), 9.9 gram benzoic acid (81 mmol), 54.0 gram diphenylether as solvent and 0,976 gram dibenzylether as 6C internal standard.

After closing and purging with CO, the reactor was heated to 140°C, under a pressure of 5.5 MPa. When this temperature was reached, a continuous supply of butadiene and methanol was started, at rates of 55 and 61 mmol.

hr^{-1} respectively. The butadiene supply was thus 28 mol/molPd/hr.

After 6.0 hours the reaction was stopped, and the mixture analyzed by gas chromatography. At the end of the reaction, the butadiene/Pd ratio was 13. Butadiene conversion was 92 %. Selectivity to methylpentenoates amounted to 95.8 %, whereby selectivity to t-M3P was 58.9%, to cis-M3P was 23.4%, to trans methyl-2-pentenoate was 5.3%, to cis-M2P was 0.3% and methyl-4-pentenoate was 0.3%. The acitivy was 25 mol/molPd/hr. 35% of the benzoic acid was converted to its methyl ester.

Example XVII

Example I was repeated using 3-pentenoic acid as the co-catalyst instead of 2,4,6-trimethyl benzoic acid. 40 molar equivalents pentenoic acid versus Pd(II) acetate were added prior to reaction, and another 20 molar equivalents were added over a period of 5.0 hours during the experiment. Butadiene and methanol were supplied with a rate of 40 and 48 molar equivalents per Pd per hour respectively. The initial and end butadiene/palladium ratios were respectively 20 and 41.

After 5 hours the conversion was 81%, and the selectivity to methyl pentenoates was 88%. The activity was 29 hr^{-1}. 44% of the 3-pentenoic acid (3 PA) was converted to its methyl ester.

Example XVIII

A 150 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.43 g (1.94 mmol) of Pd(II) acetate, 5.00 g (19.1 mmol) of triphenyl phosphine, 8.54 g (85 mmol) of 3-pentenoic acid, and 0.8 g of nonane (internal standard for GC product analysis) and 55.3 g of diphenyl ether as a solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Subsequently the temperature of the reaction mixture was raised to 140°C at a CO pressure of 4.0 MPa. After heating the reaction mixture to 140°C, and raising the pressure to 4.0 MPa, butadiene was supplied with 83 mmol per hour, and methanol with 83 mmol per hour. After one hour, 2.27 g (126 mmol) of water was injected into the autoclave under pressure. The pressure was raised to 6.0 MPa, and butadiene and methanol supply continued at the same rates as during the first hour. After an additional two hours the reaction was stopped, and the contents of the autoclave analyzed by gas-chromatographic methods.

The conversion was 80%. The selectivity to methyl pentenoates was 82%. Only 5% of 3-pentenoic acid was converted to methyl-3-pentenoate.

Example XIX

Example XVII was repeated, except that water was continuously supplied together with methanol, at rates of 78 mmol methanol and 54 mmol water per hour. Butadiene was supplied at a rate of 78 mmol per hour. After four hours the reaction was stopped.

The conversion was 75%, and the selectivity to methyl pentenoates was 79%. No esterification of 3-pentenoic acid was observed.

Example XX

Example I was repeated, using a butadiene feed of 41 mole/mole Pd/hr.

After 4.5 hours of reaction the reaction mixture was worked-up by distillation at 100°C and 0.1 mm Hg. The distillation residue was transferred back to the autoclave and an additional 6 equivalents of 2,4,6-trimethyl benzoic acid, relative to palladium, and fresh nonane as an internal standard for GC analysis were added. After raising the temperature and pressure to 140° and 6.0 MPa respectively, the butadiene and methanol feeds were resumed, as in Example 1.

Afterwards, the workup procedure was repeated and the recycle was performed again, another three times. In Table 2 the results of the subsequent cycles are listed.

TABLE 2

Run #	Conv.	Sel. to MP's	Act.
1	93	93.7	38
2	97	94.3	39
3	97	95.2	39

TABLE 2 (continued)

Run #	Conv.	Sel. to MP's	Act.
4	96	95.3	39
5	97	94.6	39

Comparative Experiment D

A 150 ml Parr autoclave, made of Hastelloy C, was filled successively with 0.38 g (1.70 mmol) of Pd(II) acetate, 2.87 g (6.7 mmol) of 1,4-bis(diphenylphosphino)-butane, 1.90 g (11.6 mmol) of trimethyl benzoic acid and 32.4 g of diphenyl ether as a solvent. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. The temperature of the reaction mixture was raised to 140°C at a CO pressure of 6.0 MPa, and subsequently butadiene and methanol supplies at a constant rate of 160 and 158 mmol per hour respectively were started, using Gilson model 302 pumps. Thus, the butadiene supply was thus 94 mol/mol Pd/hr. After 2.5 hours the reaction was stopped and the butadiene and the reaction products were analyzed by gas chromatographic methods.

The conversion was 80%. The selectivity to methyl pentenoates was 91%, consisting of trans-methyl-3-pentenoate (57%), cis-methyl-3-pentenoate (20%), trans-methyl-2-pentenoate (14%), cis-methyl-2-pentenoate (0%), and methyl-4-pentenoate (0%). The activity was 69 hr^{-1}. 20% of the trimethyl benzoic acid was converted to its methyl ester. Therefore, according to comparative Example D, using a diphosphine ligand yields unfavorable amounts of 2-pentenoate.

Examples XXI-XXVI

A 100 ml Hastelloy C mechanically stirred autoclave was flushed with carbon monoxide. It was then charged via syringe with 75 grams of a mixture of 0.24 grams of palladium acetate (1.07 mmol), 2.92 g of triphenylphosphine (11.1 mmol), a weight of organic acid to supply the mole ratio of acid/Pd shown in Table 3 and the remaining weight as diphenyl ether. The autoclave was sealed and a cold pressure of 0.07 MPa of CO was added. The autoclave was then heated with stirring to 140°C. After reaching temperature the autoclave pressure was immediately adjusted to 3.4 MPa with carbon monoxide. Pumps are used to introduce 4.00 g of butadiene (73.9 mmol) at a pumping rate of 1.80 g/hr. and 2.85 g of methanol (89.1 mmol) at a pumping rate of 1.27 g/hr. The BD/Pd-ratio's in solution were 3.5-21 mole/mole during reaction. The reaction was then allowed to run for a total of 4 hours with intermediate samples taken. The reaction was cooled, vented and the product collected.

A sample of the liquid and gas phase of each product sample was analyzed by capillary gas chromatography. The conversion achieved and the selectivity to all major products is shown in Table 3.

TABLE 3

	Acid/	% BD	Selectivity to		
Acid	Pd	Conv.	M3P	M2P	C9s
3PA	70	95	74	17	3
2PA	50	70	70	8	9
3-Butenoic	50	90	78	8	7
Nonanoic	50	89	75	11	8
CHPropionic	50	90	78	10	8

2PA = 2-pentenoic acid CHPropionic = cyclohexylpropionic acid C9s = nine-carbon dienoic esters (nonadienoic esters)

Example XXVIII

A 100 ml Hastelloy C mechanically stirred autoclave was flushed with carbon monoxide. It was then charged via syringe with 80 grams of a mixture of 0.48 grams of palladium acetate (2.14 mmol), 5.84 g of triphenylphosphine (22.3 mmol), 9.72 g of nonanoic acid (56.5 mmol) (to supply the mole ratio of acid/Pd = 27) and 64 g of diphenyl ether. The autoclave was sealed and a cold pressure of 0.07 MPa of CO was added. The autoclave was then heated with stirring to 140°C. After reaching temperature, the autoclave pressure was immediately adjusted to 3.4 MPa with carbon monoxide. Pumps are used to introduce 4.00 g of butadiene (73.9 mmol) at a pumping rate of 1.80 g/hr. and 2.40 g of

methanol (75.0 mmol) at a pumping rate of 1.27 g/hr. The BD/Pd-ratio in solution was lower than 1 mmol/mol. The reaction was then allowed to run for a total of 4 hours, while tearing intermediate samples; cooled, vented and the product collected.

A sample of the liquid and gas phase of each product sample was analyzed by capillary gas chromatography. A greater than 99% conversion of butadiene was achieved. The total selectivity to all pentenoic esters and acids was 96%, with 85% to the 3- and 4-isomers. There was also 2% selectivity to nine-carbon dienoic esters, 1.8% to octatrienes and vinylcyclohexene, and 0.2% to saturated six-carbon dimethyl esters.

Example XXVIII

A 100 ml Hastelloy C mechanically stirred autoclave was flushed with carbon monoxide. It was then charged via syringe with 79.4 grams of a mixture of 0.72 grams of palladium acetate (3.21 mmol), 8.76 g of triphenylphosphine (33.4 mmol), 9.78 g of nonanoic acid (56.8 mmol) (to supply the mole ratio of acid/Pd = 18) and 60.1 g of diphenyl ether. The autoclave was sealed and a cold pressure of 0.07 MPa of CO was added. The autoclave was then heated with stirring to 140°C. After reaching temperature, the autoclave pressure was immediately adjusted to 3.4 MPa with carbon monoxide. Pumps are used to introduce 4.00 g of butadiene (73.9 mmol) at a pumping rate of 8.1 g/hr. and 2.40 g of methanol (75.0 mmol) at a pumping rate of 5.7 g/hr. The BD/Pd-ratio in solution was 1.4 mole/mole at the end of the reaction. The reaction was then allowed to run for a total of 3 hours with intermediate samples taken. The reaction was cooled, vented and the product collected.

A sample of the liquid and gas phase of each product sample was analyzed by capillary gas chromatography. A 94% conversion of butadiene was achieved. The total selectivity to all pentenoic esters and acids was 95.5%, with 84% to the 3- and 4-isomers. There was also 1.1% selectivity to methylnonadienoates, 1.6% to methyl 2-methylbutenoate isomers.

Claims

1. A process for the preparation of pentenoic acid or a pentenoate ester by carbonylation of butadiene or a butadiene derivative in a reaction mixture in the presence of carbon monoxide and an alcohol or water and a catalyst system comprising palladium, a carboxylic acid and a monodentate phosphine ligand, characterized in that the amounts of reactants are maintained, substantially during the whole process, such that the molar ratio of butadiene or butadiene derivative to palladium in the reaction mixture is less than 70:1, the molar ratio of carboxylic acid to palladium is greater than 10:1, and the molar ratio of alcohol or water to butadiene or butadiene derivative is less than 2:1.

2. A process according to claim 1, characterized in that the ratio of butadiene or butadiene derivative to palladium is greater than 1:1.

3. A process according to claims 1-2, characterized in that the ratio of butadiene or butadiene derivative to palladium is less than 50:1.

4. A process according to claims 1-3, characterized in that the molar ratio of alcohol or water to butadiene or butadiene derivative is between 1:1 and 1.5:1.

5. Process according to any one of claims 1-4, characterized in that the process is performed continuously or semicontinuously.

6. A process according to claims 5, characterized in that the amounts of reactants are maintained during more than 90% of the process as expressed in residence time or reaction time.

7. Process according to any one of claims 1-6, characterized in that the carboxylic acid is a sterically hindered carboxylic acid having a pKa between 2 and 5.0, measured in an aqueous solution of 18°C.

8. Process according to claim 7, characterized in that the carboxylic acid is a sterically hindered benzoic acid.

9. Process according to any one of claims 1-6, characterized in that the carboxylic acid is a pentenoic acid or a nine-carbon carboxylic acid.

10. A process according to claims 1-6, characterized in that said process is performed continuously, and that any esterification product of the carboxylic acid formed during the carbonylation is hydrolyzed to the carboxylic acid in a separate step; and the carboxylic acid is reused in the continuously performed carbonylation.

11. A process according to claims 1-9, wherein the alcohol is methanol or ethanol.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 20 0391

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP-A-0 271 145 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * page 3, line 32 - page 4, line 18 * * page 6, line 6 - line 16 * * page 7, line 29 - line 33 * * page 8, line 34 - page 9, line 16 * * page 11 - page 14; examples 1-3,5 * * page 15 - page 18; claims * ---	1,2,4,11	C07C67/38 C07C69/533
Y	EP-A-0 577 205 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * page 3, line 13 - line 36 * * page 4, line 51 - page 5, line 15 * * page 4 - page 5; examples 1-10 * * page 6 - page 7; claims * ---	1,2,4,7,8,11	
Y	EP-A-0 273 489 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) * page 3, line 17 - line 40 * * page 4, line 32 - line 50 * * page 5, line 11 - line 22 * * page 7; examples 5,7 * * page 8 - page 9; claims *	1,2,4,7,8,11	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C07C
D	& US-A-5 028 734 -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	9 May 1996	Kinzinger, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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